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<p>(54) Title: CLATHRATE HYDRATE DISSOCIATION POINT DETECTION AND MEASUREMENT</p> <p>(57) Abstract</p> <p>Apparatus and method for detecting the formation and dissociation of gas or clathrate hydrates in a fluid. The apparatus used comprises a piezoelectric crystal sensor and a signal analyser. The crystal sensor has a deposition surface in contact with the fluid. Under a range of pressures and/or temperatures the resonant frequency or an electrical parameter dependent on the resonant frequency of the piezoelectric sensor is measured. There is a step change in the resonant frequency which occurs upon the formation or dissociation of a clathrate hydrate on the deposition surface, so that the formation or dissociation of said clathrate hydrate may be detected.</p>			

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1 CLATHRATE HYDRATE DISSOCIATION POINT DETECTION AND
2 MEASUREMENT

3

4 The present invention relates to the detection of the
5 dissociation of clathrate hydrates and in particular,
6 but not exclusively, to the measurement of pressures
7 and corresponding temperatures at which clathrate
8 hydrates are found to dissociate.

9

10 Clathrate hydrates of gases are formed when, under
11 favourable temperature and pressure conditions, gas
12 molecules become encapsulated in crystalline structures
13 of water. The water forms a cage-like structure around
14 guest molecules. Chlorine hydrates were first
15 discovered in 1810 and following this many compounds
16 which form clathrate hydrates have been identified. In
17 1934 it was discovered that gas clathrate hydrates were
18 causing blocking of natural gas transmission lines and
19 for this reason research aimed at understanding and
20 resolving this problem was initiated and continues
21 today. Apart from being considered as a problem in the
22 oil industry, clathrate hydrates are considered
23 important for a number of reasons such as a potential
24 source of energy, and for use in processes such as
25 desalination and gas transportation.

1 Clathrate hydrates, especially in the oil industry, are
2 often referred to as gas hydrates, or simply as
3 hydrates. Gas hydrates of interest, particularly with
4 respect to producing, transporting and processing of
5 natural gas and petroleum fluids, are composed of water
6 and the following eight guest molecules: methane,
7 ethane, propane, isobutane, normal butane, nitrogen,
8 carbon dioxide and hydrogen sulphide. Other guest
9 molecules capable of forming clathrate hydrates include
10 ethane, nitrous oxide, acetylene, vinyl chloride,
11 methyl bromide, ethyl bromide, cyclopropane, methyl
12 mercaptan, sulphur dioxide, argon, krypton, oxygen,
13 xenon, trimethylene oxides and others. Clathrate
14 hydrate formation is a possibility wherever water
15 exists in the presence of such molecules, both
16 naturally and artificially, at temperatures above 0°C
17 and below 0°C, when pressure is elevated.
18

19 It is primarily due to their crystalline, insoluble,
20 non-flowing nature that hydrates have been of interest
21 to industry. They are a source of problems, because
22 they block transmission lines, plug Blow Out
23 Preventers, jeopardize the foundations of deepwater
24 platforms and pipelines, collapse tubing and casing,
25 and foul process heat exchangers and expanders. Common
26 methods of preventing hydrate formation are the
27 regulation of pipeline water content, the use of
28 special drilling mud compositions and the injection of
29 Large quantities of methanol into pipelines. All these
30 methods are costly and complex, so there is a need to
31 know more about the likelihood of clathrate formation
32 in a particular sample.

33
34 The point (in terms of pressure and temperature) at
35 which, in a system containing a clathrate hydrate, the
36 hydrate dissociates is known as the dissociation point.

1 The pressure at which a clathrate hydrate dissociates
2 at a given temperature is referred to as the
3 dissociation pressure (DP) for that temperature, while
4 the temperature at which the hydrate dissociates for a
5 given pressure is referred to as the dissociation
6 temperature (DT) for that pressure. The DP and DT are
7 important factors to be determined in order to identify
8 and characterise the nature and properties of any
9 clathrate hydrate.

10
11 Previously, the DP or DT of a given hydrate has been
12 determined using methods dependent on visual
13 identification of clathrate formation/dissociation,
14 which are prone to human error and are inherently
15 inaccurate. Measurements of the DT have also been made
16 by mixing a test fluid with water, supercooling the
17 mixture till the clathrate is formed, and then slowly
18 warming the clathrate and detecting and/or measuring
19 the increase in pressure which results from gas
20 molecules escaping from inside the clathrate upon its
21 dissociation. The latter method suffers from the
22 problem of being extremely time consuming since the
23 time taken for a system containing a sufficiently large
24 sample of the (solid phase) clathrate to reach
25 equilibrium at each desired temperature measurement is
26 significant, in some cases a number of weeks.
27

28 It is an aim of the present invention substantially to
29 avoid or minimise one or more of the foregoing
30 disadvantages.

31
32 According to a first aspect of the present invention we
33 provide an apparatus suitable for use in detecting the
34 formation of, and/or the onset of dissociation of,
35 clathrate hydrates, the apparatus comprising: a
36 piezoelectric crystal sensor which is formed and

1 arranged to resonate at a variable frequency which is
2 dependent upon a mass loading on a deposition surface
3 thereof; and signal analyser means formed and arranged
4 for monitoring, in use of the apparatus, directly or
5 indirectly, change in the resonant frequency of the
6 piezoelectric crystal sensor while one of the
7 temperature and pressure of a test sample in contact
8 with the deposition surface of the sensor is varied, so
9 as to detect a substantial change in said resonant
10 frequency occurring upon the formation or dissociation
11 of a clathrate hydrate on the deposition surface,
12 whereby the formation or dissociation of said clathrate
13 hydrate may be detected.

14

15 One advantage of the apparatus of the invention is that
16 it enables the dissociation (or the formation) of
17 clathrate hydrates to be detected very accurately.
18 Unlike the aforementioned prior art, the invention does
19 not rely on visual identification methods, or the
20 detection of small pressure increases.

21

22 According to a second aspect of the invention we
23 provide an apparatus for measuring dissociation point
24 temperatures and pressures of clathrate hydrates, the
25 apparatus comprising: a piezoelectric crystal sensor
26 which is formed and arranged to resonate at a variable
27 frequency which is dependent upon a mass loading on a
28 deposition surface thereof;
29 a pressure vessel having a pressure chamber defined
30 therein, said piezoelectric crystal sensor being
31 mounted in the pressure chamber, and the pressure
32 vessel having inlet means via which a test fluid may be
33 introduced into the pressure chamber of the vessel;
34 temperature control means for controlling the
35 temperature in the pressure chamber;
36 pressure control means for controlling the pressure in

1 the chamber;
2 signal analyser means formed and arranged for
3 monitoring, in use of the apparatus, directly or
4 indirectly, change in the resonant frequency of the
5 piezoelectric crystal while one of the temperature and
6 pressure of test fluid in contact with the deposition
7 surface of the sensor is varied, so as to detect a
8 substantial change in said resonant frequency occurring
9 upon the formation or dissociation of a clathrate
10 hydrate on the deposition surface, whereby the
11 formation or dissociation of said clathrate hydrate may
12 be detected; and temperature measuring means and
13 pressure measuring means for measuring the temperature
14 and pressure in the chamber at least when the
15 dissociation of said clathrate hydrate is detected.
16

17 An advantage of the apparatus of present invention is
18 that only a relatively small amount of the test fluid
19 is required since only a small amount of clathrate
20 hydrate need be formed in the apparatus of the
21 invention in comparison with the prior art techniques
22 which rely on visual identification of clathrate
23 formation and dissociation, or detection of pressure
24 changes due to clathrate hydrate
25 formation/dissociation, and thus require much larger
26 amounts of clathrate hydrates to be present. In
27 consequence, another advantage of the apparatus is that
28 it enables the DT or DP to be measured relatively
29 quickly in comparison with the afore-mentioned prior
30 art methods which required relatively large samples of
31 clathrate hydrate (in which equilibrium conditions for
32 a given temperature and pressure can take a very long
33 time to reach) in order for effects occurring at the
34 dissociation point to be detected.

35

36 Said substantial change in the resonant frequency

1 occurring in the resonant frequency may be of the order
2 of a few hundred to a few thousand Hertz. The
3 magnitude of the change may be greater or smaller than
4 this, though, depending on the amount of hydrate formed
5 on the crystal and/or where on the crystal surface the
6 hydrate is situated.

7

8 Advantageously, the temperature and pressure measuring
9 means are formed and arranged for continuously
10 measuring temperature and pressure in the pressure
11 chamber, in use of the apparatus.

12

13 The piezoelectric crystal sensor preferably comprises a
14 quartz crystal microbalance (QCM). The QCM
15 conveniently comprises an AT-cut quartz crystal
16 sandwiched between excitation electrodes to which a
17 driving signal may be applied to generate a transverse
18 shear wave across the thickness of the crystal. Such a
19 QCM can be made to oscillate even when immersed in
20 fluid (gas or liquid) and will resonate at a frequency
21 which is dependent, among other things, on the mass
22 loading on the crystal. Any change in the mass load on
23 the crystal will change the resonant frequency of the
24 QCM. When a clathrate hydrate forms from a mixture of
25 ice and test fluid on the so-called deposition surface
26 of the crystal, the mass load on the crystal will
27 change significantly and this will, in turn,
28 significantly change the resonant frequency of the QCM.
29 Similarly, a significant change in the resonant
30 frequency will occur when a clathrate hydrate present
31 on the deposition surface of the crystal dissociates.

32

33 A further advantage of the present invention is that
34 if, due to a change in the structure of a clathrate
35 hydrate being analysed, a density change in the hydrate
36 occurs, the apparatus according to the invention may be

1 capable of detecting and measuring the point, in terms
2 of pressure and temperature, at which this structural
3 change takes place. Moreover, if more than one
4 clathrate hydrate structures is formed on the
5 deposition surface of the crystal, it may be possible
6 to detect and/or measure the dissociation point
7 temperature/pressure for each such structure.

8

9 The signal analyser means is preferably adapted to
10 control the driving signal supplied to the excitation
11 electrodes and may be adapted to, for example, analyse
12 the phase of an electrical impedance or gain of the
13 sensor so as to detect a resonant condition of the
14 sensor (occurring at a resonant frequency of the
15 sensor). Similarly, the resonant condition could be
16 detected by monitoring, for example, current, voltage
17 or electrical conductance of the sensor so as to detect
18 a resonant condition thereof. In use of the apparatus,
19 the signal analyser means is advantageously adapted to
20 produce and detect a resonant condition of the sensor
21 at a predetermined number of different pressures, or
22 temperatures, in the pressure chamber of the pressure
23 vessel.

24

25 The analyser means is preferably adapted to measure,
26 and conveniently also to store or record, the value of
27 the (driving) signal frequency, and/or one or more of
28 the sensor current, voltage and conductance, at each
29 detected resonant condition of the sensor. Change in
30 the resonant frequency may thus be monitored directly,
31 or alternatively indirectly by monitoring change in the
32 values of, for example, current, voltage or
33 conductance, at resonant frequency.

34

35 Where the piezoelectric crystal sensor comprises a QCM,
36 the quartz crystal incorporated therein is preferably

1 an unpolished quartz crystal. This had the advantage
2 of increasing the likelihood that hydrate(s) which have
3 formed will adhere to the crystal.

4

5 In use of the apparatus, test fluid to be analysed is
6 injected or other wise introduced into the pressure
7 chamber so as to surround the piezoelectric crystal
8 sensor. At least a small amount of water is preferably
9 introduced onto said deposition surface of the crystal
10 sensor and frozen prior to introduction of the test
11 fluid to the pressure chamber, in order to allow
12 clathrate hydrates to form. This water may be
13 introduced by, for example, placing one or more drops
14 of water onto the deposition surface of the crystal
15 sensor and lowering the temperature in the pressure
16 chamber so as to freeze the water. The pressure
17 control means may conveniently comprise valve means on
18 the inlet means of the pressure vessel for controlling
19 the injection or release of fluid into or out of the
20 pressure chamber. The pressure vessel may further
21 include outlet means via which fluid contents of the
22 pressure chamber may exit therefrom. Alternatively, or
23 additionally, the pressure control means may comprise
24 pump means for compressing or evacuating fluid in/form
25 the pressure chamber. Pump means may be provided for
26 connection to the outlet means, for evacuating the
27 pressure chamber.

28

29 The temperature control means may comprise a water
30 jacket surrounding the pressure vessel. Additionally,
31 or alternatively, the temperature control means may
32 include a heat sink.

33

34 The apparatus conveniently includes a pressure vessel
35 mounting means incorporating a pivotal mounting for the
36 pressure vessel, whereby the pressure vessel is

1 pivotally mounted to allow rotation of the vessel, in
2 use of the apparatus, so as to mix the fluid contents
3 of the vessel. Rotating the vessel can reduce the time
4 taken for the contents of the pressure vessel to reach
5 equilibrium.

6

7 According to a third aspect of the invention we provide
8 a method of measuring dissociation temperatures and
9 dissociation pressures of a clathrate hydrate, the
10 method comprising the steps of:

- 11 a) providing, in a pressure chamber of a pressure
12 vessel, a piezoelectric crystal sensor which is formed
13 and arranged to resonate at a variable frequency which
14 is dependent on a mass loading on a deposition surface
15 thereof;
- 16 b) depositing a small amount of water on said sensor
17 deposition surface;
- 18 c) lowering the temperature in the pressure chamber
19 below freezing so as to freeze said small amount of
20 water;
- 21 d) evacuating the pressure chamber and subsequently
22 introducing therein a test fluid;
- 23 e) controlling the temperature and pressure in the
24 pressure chamber so as to achieve clathrate hydrate
25 formation on the deposition surface of the sensor;
- 26 f) monitoring, directly or indirectly, change in the
27 resonant frequency of the piezoelectric crystal sensor
28 while said temperature and pressure are controlled, so
29 as to detect a substantial change in said resonant
30 frequency which occurs upon formation of said clathrate
31 hydrate, thereby to detect the formation of said
32 clathrate hydrate;
- 33 g) varying one of the temperature and pressure in the
34 pressure chamber, preferably in a step-wise manner, so
35 as to cause dissociation of the clathrate hydrate,
36 while maintaining the other one of the temperature and

1 pressure substantially constant at a predetermined
2 value;

3 h) monitoring, directly or indirectly, change in the
4 resonant frequency of the piezoelectric crystal sensor
5 while said one of the temperature and pressure is
6 varied, so as to detect a substantial change in said
7 resonant frequency which occurs upon dissociation of
8 the clathrate hydrate, thereby to detect the
9 dissociation of said clathrate hydrate; and

10 j) measuring the magnitude of the varying one of the
11 temperature and pressure when the dissociation of said
12 clathrate hydrate is detected, and the magnitude of the
13 one of the temperature and pressure which is held
14 substantially constant, the measured magnitudes
15 representing one of: the dissociation temperature of
16 said clathrate hydrate at a predetermined pressure, and
17 the dissociation pressure of said clathrate hydrate at
18 a predetermined temperature.

19

20 Said small amount of water may be deposited on the
21 sensor deposition surface in a number of possible ways.
22 It is hereby expressly stated that steps (a) and (b) of
23 the above method may be carried out in any order. For
24 example, one or more drops of water may be placed on
25 the deposition surface of the sensor prior to placing
26 the sensor in the pressure chamber of the pressure
27 vessel. Alternatively, water in the form of drops,
28 mist, or liquid could be introduced into the pressure
29 chamber once the sensor has been placed therein, as
30 long as it can be ensured that at least some water will
31 be deposited on the sensor deposition surface. The
32 crystal may additionally be coated with a hygroscopic
33 material for absorbing moisture introduced into the
34 pressure chamber.

35

36 Using the above-described method, the dissociation

1 temperature (DT) at a given pressure, or alternatively
2 the dissociation pressure (DP) at a given temperature,
3 may be measured.

4

5 Preferably, the temperature and pressure in the
6 pressure chamber are continuously measured,
7 conveniently throughout steps (c) to (j) of the method.

8

9 The detection of said substantial change in the
10 resonant frequency may be achieved by recording
11 monitored values of the resonant frequency or, for
12 example, current, voltage or conductance at resonant
13 frequency, and the corresponding varying temperature or
14 pressure values, in graphical form, thereby recording
15 the substantial change in the resonant frequency, or
16 the nominated other electrical property at resonant
17 frequency, occurring at the DT or DP.

18

19 The above-described apparatus and method(s) are
20 intended in particular, but exclusively, for laboratory
21 use. e.g. for the determination of dissociation
22 temperatures and pressure of sample clathrate hydrates.
23 It is envisaged that the apparatus could, nevertheless,
24 be used in certain in situ applications, for example in
25 monitoring applications where, for safety reasons or
26 other operating considerations, the detection of the
27 formation of clathrate hydrates is desirable. This
28 could be the detection of the formation of clathrate
29 hydrates in an underground gas pipe, for example,
30 and/or measurement of the dissociation temperature or
31 pressure of clathrate hydrates present in a system in
32 which one of the temperature and pressure is varying
33 while the other one remains substantially constant.

34

35 Preferred embodiments of the invention will now be
36 described by way of example only and with reference to

1 the accompanying drawings in which:
2 Fig. 1(a) is a schematic side view (enlarged) of a
3 quartz crystal microbalance (QCM);
4 Fig. 1(b) is an end view of the arrangement of the
5 quartz crystal and the electrodes of the QCM of
6 Fig. 1(a);
7 Fig. 2 is a schematic diagram of the equivalent
8 electrical circuit representing the electrical
9 behaviour of the QCM;
10 Fig. 3 is a cross-sectional side view through an
11 apparatus 12 according to the invention for detecting
12 and measuring clathrate hydrate dissociation points;
13 Fig. 4 shows graphs of resonant frequency vs.
14 temperature, and conductance at resonant frequency
15 versus temperature, obtained using the apparatus of
16 Fig. 3, illustrating the dissociation of a clathrate
17 hydrate formed from methane and isopentane, at
18 8.28MPascals; and
19 Fig. 5 is a graph of pressure vs. temperature at the
20 hydrate phase boundary for ethane hydrate, comparing
21 theoretical data with experimental data obtained using
22 the apparatus of Fig. 3.
23
24 Fig. 1(a) shows schematically a typical Quartz Crystal
25 Microbalance (QCM) 1. The QCM comprises an AT-cut
26 polished quartz crystal 2 sandwiched between two gold
27 excitation electrodes 3 (as shown in detail in
28 Fig. 1(b)) that generate a transverse shear wave across
29 the thickness of the quartz crystal (when a driving
30 electrical signal is applied to the electrodes). The
31 crystal 2 has an inherent resonant frequency at 5MHz.
32 The crystal 2 is mounted by means of two connecting
33 wires 6 connected to respective ones of the electrodes
34 3, to a mounting base 4, as shown. Driving signals are
35 applied to the connecting wires 6 via conducting pins 5
36 which extend through the mounting base 4.

1 Fig. 2 shows the elements of an equivalent electrical
2 circuit 10 which the resonant electrical behaviour of
3 the QCM imitates. As shown, the equivalent electrical
4 circuit 10 comprises a resistor R, capacitor C and
5 inductor L, all in series, which are in parallel with
6 an additional capacitance Co which is the static
7 capacitance of the quartz crystal.

8

9 Fig. 3 shows a cross-section through an apparatus 12
10 according to a preferred embodiment of the invention.
11 The apparatus 12 comprises a stainless steel pressure
12 vessel 14 defining an internal pressure chamber 16 of
13 volume 40 cubic centimetres (cc). A QCM 18 is mounted
14 in the pressure chamber 16. The two electrodes 17
15 (only one shown) of the QCM are gold, are bonded to the
16 surface of the QCM crystal 19, and are connected, via
17 high pressure vessel 14, to an HP 4194A impedance/gain
18 phase analyser 26 (indicated in block form only)
19 located remote from the pressure vessel. The pressure
20 vessel has a sample inlet 28 communicating with the
21 chamber 16 via which inlet test fluid may be introduced
22 to the chamber 16. An outlet 30 is also provided in
23 the pressure vessel via which fluids may exit from the
24 chamber 16. The pressure vessel 14 is mounted on a
25 pivot (not shown) to allow for rotation of the vessel,
26 and thus mixing of the contents of the vessel, so as to
27 help in achieving equilibrium of the contents of the
28 pressure chamber 16. The pressure vessel 14 is also
29 surrounded by a water jacket 28 (indicated in broken
30 lines) for use in controlling the temperature of the
31 contents of the pressure chamber 16. A temperature
32 sensor (not shown) of the platinum resistance probe
33 type is provided in the apparatus, in the water jacket
34 28, for continuously monitoring the temperature of the
35 water jacket (which is substantially the same, or
36 closely approximates to, the temperature in the

1 pressure chamber). A pressure sensor (not shown) in
2 the form of a strain gauge transducer is located in a
3 branch off the outlet 30 of the pressure vessel and is
4 arranged to continuously monitor the pressure therein.
5

6 The pressure vessel 14, as shown in Fig. 3, in fact
7 comprises two separate portions: a main portion 32
8 having the inlet 28 and largely defining the chamber
9 16, and a lid portion 34 having the electric feed
10 throughs 22, 24, to which the QCM is attached, and the
11 outlet 30. The lid portion 34 is bolted to the main
12 portion 32, the recessed bolt holes 31, 33 being shown
13 in Fig. 3. In use of the apparatus, a drop of water is
14 placed on one surface of the quartz crystal 19,
15 hereinafter referred to as "the deposition surface",
16 prior to assembling the lid portion 34 to the main
17 portion 32. After bolting the two portions of the
18 pressure vessel together, thereby closing the chamber
19 16 except to fluids entering or leaving therefrom via
20 the inlet 28 and outlet 30 respectively, the
21 temperature in the chamber 16 is lowered below 0°C,
22 using the water jacket, in order to freeze the drop of
23 water. The chamber 16 is then evacuated using a vacuum
24 pump (not shown) connected to the outlet 30 and a
25 sample of test fluids is then injected or pumped into
26 the chamber 16 via the inlet 28. The chamber pressure
27 P and temperature T are then adjusted using the water
28 jacket and by releasing and/or injecting test fluid
29 into or out of the chamber until conditions favourable
30 for clathrate hydrate formation are achieved. The
31 formation of such hydrates is obvious as it causes
32 significant changes in the resonant frequency, or other
33 electrical properties such as conductance at resonant
34 frequency, which changes can be detected using the
35 phase analyser 26.

Once the formation of clathrate hydrate(s) on the QCM has been detected, dissociation point measurements can then be obtained by, for example, raising the temperature step-wise in the chamber, while keeping the pressure therein substantially constant, and using the phase analyser 26 to monitor the resonant frequency, and/or conductance at resonant frequency, of the QCM at each temperature and to detect any significant changes therein, signalling dissociation of the clathrate hydrate. Alternatively, the temperature may be kept substantially constant while the pressure in the chamber is varied in a step-wise manner and the resonant frequency and/or conductance at resonant frequency is monitored.

15

Fig. 4 illustrates graphically the detection and measurement of the dissociation temperature, at 8.28 MPascals pressure, for a clathrate hydrate formed from a mixture of methane and isopentane. The temperature in the chamber 16 was varied in a step-wise manner and at each temperature the resonant frequency f_R and the conductance at resonant frequency c_R of the QCM was measured by the phase analyser 26. By plotting a graph of resonant frequency f_R against pressure P , and/or a graph of Conductance c_R at resonant frequency against pressure P , the dissociation of the clathrate hydrate can be seen clearly in the graph as a significant change in the resonant frequency (a change of approx. 2000Hz), and a significant change in the Conductance at resonant frequency (a change of approx. 550 μ S), occurring substantially at the dissociation temperature (approx. 284 Kelvin). Fig. 5 is a graph of pressure P vs. temperature T plotted using theoretically calculated values for ethane hydrate in the region of the liquid/gas phase boundary. Experimental points obtained from the experimental data collected with the

1 apparatus of the invention are indicated on the graph
2 in Fig. 5 and it can be seen that there is a good
3 agreement between the theoretical and experimental
4 data.

5

6 In a further possible embodiment of the invention, the
7 measurements of resonant frequency f_R , and Conductance
8 at resonant frequency c_R , are recorded by a recording
9 device 36 (e.g. a printer, or a microprocessor with a
10 VDU) connected to the phase analyser 26, as shown in
11 broken lines in Fig. 3.

12

13 The invention has other applications, apart from those
14 described above. The method of measuring the hydrate
15 dissociation point of the present invention may be used
16 for the rapid screening of chemicals for both hydrate
17 inhibition and hydrate promotion. Tests were carried
18 out with hydrates formed with methane and cyclopentane,
19 and gave following results. Forming hydrates from
20 water resulted in a drop in conductance of around 90
21 micro Siemens. Forming hydrates from melting ice and
22 from water with asphaltenes present gave a drop in
23 conductance of around 476 micro Siemens. The drop is
24 related to the conductance measurement when water or
25 water with asphaltene is on the QCM with no hydrate
26 formation. These results show that the formation of
27 hydrates from melting ice or from water with
28 asphaltenes is more efficient. This increase in
29 efficiency is due to the number of nucleation sites in
30 the droplet of water.

31

32 The rate of drop in conductance measured in the method
33 of the invention can also be used to show the rate of
34 hydrate formation. The method and apparatus can be
35 used to determine rapidly the efficiency of proposed
36 hydrate inhibitors and/or promoters, using small

1 amounts of sample and with real fluids.
2

3 The small volume of sample needed represents a real
4 advantage over prior art methods, which typically would
5 need a sample of 50cc of fluid. The present invention
6 can be carried out with a small sample, even a drop, on
7 the surface of the crystal. The development of smaller
8 crystal sensors will make the detection of hydrate
9 dissociation points possible with samples whose mass is
10 measured in nanograms.

11
12 Further tests with hydrates using the method of the
13 invention have shown that where the cavity occupancy
14 has an influence on the density of the hydrates formed,
15 then this influence can be detected. For example, for
16 hydrates formed from methane and isopentane, below the
17 quintuple point structure H hydrates are formed,
18 composed of water cages with methane and isopentane
19 molecules filling the cavities. Above the quintuple
20 point only structure I hydrates are formed with methane
21 filling the cavities. There is a significant density
22 difference between the two types of hydrates. By
23 shifting the temperature and pressure above and below
24 the quintuple point, the change in structure of the
25 hydrates can be detected, since it results in a
26 significant change in the conductance reading at
27 resonant frequency.

28
29 The invention can find an application in the evaluation
30 of surface treatments designed to prevent hydrates
31 sticking.

32
33 These and other modifications and improvements can be
34 incorporated without departing from the scope of the
35 invention.

1 CLAIMS

2

3 1. An apparatus suitable for use in detecting the
4 formation of, and/or the onset of dissociation of,
5 clathrate hydrates, the apparatus comprising:

6 a piezoelectric crystal sensor which is formed and
7 arranged to resonate at a variable frequency which is
8 dependent upon a mass loading on a deposition surface
9 thereof; and

10 signal analyser means formed and arranged for
11 monitoring, in use of the apparatus, directly or
12 indirectly, change in the resonant frequency of the
13 piezoelectric crystal sensor while one of the
14 temperature and pressure of a test sample in contact
15 with the deposition surface of the sensor is varied, so
16 as to detect a substantial change in said resonant
17 frequency occurring upon the formation or dissociation
18 of a clathrate hydrate on the deposition surface,
19 whereby the formation or dissociation of said clathrate
20 hydrate may be detected.

21

22 2. Apparatus according to Claim 1 further comprising:

23 a pressure vessel having a pressure chamber
24 defined therein, said piezoelectric crystal sensor
25 being mounted in the pressure chamber, and the pressure
26 vessel having inlet means via which a test fluid may be
27 introduced into the pressure chamber of the vessel.

28

29 3. Apparatus according to Claim 1 or 2 further
30 comprising:

31 temperature control means for controlling the
32 temperature in the pressure chamber.

33

34 4. Apparatus according to any preceding claim further
35 comprising:

36 pressure control means for controlling the

1 pressure in the chamber.

2

3 5. Apparatus according to any preceding claim further
4 comprising:

5 at least one of temperature measuring means and
6 pressure measuring means for measuring the temperature
7 and/or pressure in the chamber at least when the
8 dissociation of said clathrate hydrate is detected.

9

10 6. Apparatus according to any preceding claim wherein
11 the piezoelectric crystal sensor is an acoustic wave
12 sensor selected from the group consisting of thickness-
13 shear-mode (TSM) devices, surface-acoustic-wave (SAW)
14 devices, acoustic-plate-mode (APM) devices and
15 flexural-plate-wave (FPW) devices.

16

17 7. Apparatus according to Claim 6 wherein the
18 piezoelectric crystal sensor is a quartz crystal
19 microbalance comprising an AT-cut quartz crystal
20 sandwiched between excitation electrodes to which a
21 driving signal may be applied to generate a transverse
22 shear wave across the thickness of the crystal.

23

24 8. Apparatus according to Claim 7 wherein the signal
25 analyser means is adapted to control the driving signal
26 supplied to the excitation electrodes.

27

28 9. Apparatus according to Claims 7 or 8 wherein the
29 signal analyser means is adapted to analyse the phase
30 of an electrical impedance or gain of the sensor so as
31 to detect a resonant condition of the sensor which
32 occurs at a resonant frequency of the sensor.

33

34 10. Apparatus according to Claim 9 wherein the
35 resonant condition is detected by monitoring current,
36 voltage or electrical conductance of the sensor.

- 1 11. Apparatus according to any preceding claim wherein
2 the signal analyser means comprises control means
3 adapted to produce and detect a resonant condition of
4 the sensor at a predetermined number of different
5 pressures, or temperatures, of the fluid in contact
6 with the sensor.
- 7
- 8 12. Apparatus according to any preceding claim wherein
9 the signal analyser means comprises a driving signal
10 generator and measurement means adapted to measure the
11 frequency of the driving signal and/or one or more of
12 the sensor current, voltage and conductance, at each
13 detected resonant condition of the sensor.
- 14
- 15 13. Apparatus according to Claim 12 wherein the signal
16 analyser means comprises monitoring means adapted to
17 monitor the change in the resonant frequency.
- 18
- 19 14. Apparatus according to Claim 13 wherein said
20 monitoring means monitors the change in resonant
21 frequency by monitoring the change in the values of
22 current, voltage or conductance, at resonant frequency.
- 23
- 24 15. Apparatus according to any of Claims 12 to 14
25 wherein the signal analyser means comprises data
26 storage means for storing and/or recording the value of
27 the driving signal frequency, and/or one or more of the
28 sensor current, voltage and conductance, at each
29 detected resonant condition of the sensor.
- 30
- 31 16. Apparatus according to any preceding claim wherein
32 the signal analyser means comprises computational means
33 which recognises and calculates the point at which
34 there is a discontinuity in the change of resonant
35 frequency with changing temperature or changing
36 pressure.

- 1 17. Apparatus according to Claim 16 wherein the
2 discontinuity is a step change in the resonant
3 frequency or a substantial change in the rate of change
4 of resonant frequency with changing temperature or
5 changing pressure.
- 6
- 7 18. Apparatus according to any preceding claim wherein
8 the piezoelectric crystal sensor comprises a quartz
9 crystal having an unpolished quartz crystal surface, to
10 promote the formation of crystals on said surface.
- 11
- 12 19. Apparatus according to any preceding claim further
13 comprising means for introducing a small amount of
14 water onto said deposition surface of the crystal
15 sensor.
- 16
- 17 20. Apparatus according to any preceding claim further
18 comprising valve means for controlling the injection or
19 release of fluid into or out of the pressure chamber.
- 20
- 21 21. Apparatus according to any preceding claim further
22 comprising outlet means via which fluid contents of the
23 pressure chamber may exit therefrom.
- 24
- 25 22. Apparatus according to any preceding claim further
26 comprising pump means for compressing or evacuating
27 fluid in or from the pressure chamber.
- 28
- 29 23. Apparatus according to any preceding claim further
30 comprising a water jacket surrounding the pressure
31 vessel.
- 32
- 33 24. Apparatus according to any preceding claim further
34 comprising a heat sink.
- 35
- 36 25. Apparatus according to any preceding claim wherein

1 the pressure chamber is pivotally mounted to allow
2 rotation of the chamber, in use of the apparatus, so as
3 to mix the fluid contents of the chamber.

4

5 26. A method of measuring dissociation temperatures
6 and dissociation pressures of a clathrate hydrate, the
7 method comprising the steps of:

- 8 a) providing a piezoelectric crystal sensor which is
9 formed and arranged to resonate at a variable frequency
10 which is dependent on a mass loading on a deposition
11 surface thereof;
- 12 b) introducing a test fluid into contact with the
13 deposition surface of the sensor;
- 14 c) controlling the temperature and/or pressure of the
15 test fluid so as to achieve clathrate hydrate formation
16 on the deposition surface of the sensor;
- 17 d) monitoring, directly or indirectly, change in the
18 resonant frequency of the piezoelectric crystal sensor
19 while said temperature and/or pressure are controlled,
20 so as to detect a substantial change in said resonant
21 frequency which occurs upon formation of said clathrate
22 hydrate, thereby to detect the formation of said
23 clathrate hydrate;
- 24 e) varying one of the temperature and pressure in the
25 pressure chamber, preferably in a step-wise manner, so
26 as to cause dissociation of the clathrate hydrate,
27 while maintaining the other one of the temperature and
28 pressure substantially constant at a predetermined
29 value;
- 30 f) monitoring, directly or indirectly, change in the
31 resonant frequency of the piezoelectric crystal sensor
32 while said one of the temperature and pressure is
33 varied, so as to detect a substantial change in said
34 resonant frequency which occurs upon dissociation of
35 the clathrate hydrate, thereby to detect the
36 dissociation of said clathrate hydrate; and

1 g) measuring the magnitude of the varying one of the
2 temperature and pressure when the dissociation of said
3 clathrate hydrate is detected, and the magnitude of the
4 one of the temperature and pressure which is held
5 substantially constant, the measured magnitudes
6 representing one of: the dissociation temperature of
7 said clathrate hydrate at a predetermined pressure, and
8 the dissociation pressure of said clathrate hydrate at
9 a predetermined temperature.

10

11 27. Method according to Claim 26 wherein the crystal
12 sensor is in a pressure chamber and the test fluid is
13 introduced into the pressure chamber .

14

15 28. Method according to Claim 27 wherein the method
16 includes the following steps before or after step a):
17 a1) depositing a small amount of water on said sensor
18 deposition surface;
19 a2) lowering the temperature in the pressure chamber
20 below freezing so as to freeze said small amount of
21 water; and
22 a3) evacuating the pressure chamber and subsequently
23 introducing therein a test fluid.

24

25 29. Method according to Claim 27 or 28 wherein water
26 in the form of drops, mist, or liquid is be introduced
27 into the pressure chamber after the sensor has been
28 placed therein.

29

30 30. Method according to one of Claims 27 to 29,
31 wherein the crystal surface is coated with a
32 hygroscopic material for absorbing moisture introduced
33 into the pressure chamber.

34

35 31. Method according to one of Claims 26 to 30 in.
36 which the detection of said substantial change in

1 resonant frequency and/or rate of change of resonant
2 frequency is achieved by recording monitored values of
3 said resonant frequency.

4

5 32. Method according to Claim 31 in which the
6 detection of said substantial change in resonant
7 frequency and/or rate of change of resonant frequency
8 is achieved by recording monitored values of an
9 electrical parameter dependent upon said resonant
10 frequency, said parameter being selected from the group
11 comprising current, voltage or conductance.

12

13 33. Method according to any of claims 26 to 32 further
14 comprising the step of measuring the magnitude of the
15 varying one of the temperature and pressure when said
16 significant change in resonant frequency and/or rate of
17 change in resonant frequency occurs, and the magnitude
18 of the other one of the temperature and pressure which
19 is held substantially constant.

20

21 34. Method according to Claim 33, wherein the
22 dissociation temperature (DT) at a given pressure is
23 calculated.

24

25 35. Method according to Claim 33, wherein the
26 dissociation pressure (DP) at a given temperature is
27 calculated.

28

29 36. Method according to any of Claims 26 to 35, in
30 which there is used an apparatus according to any one
31 of Claims 1 to 25.

32

1 / 3

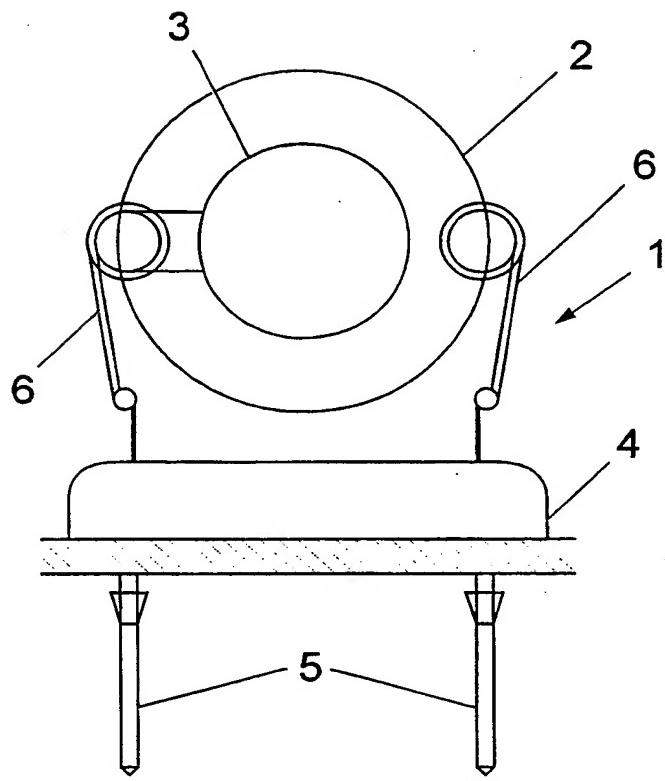


Fig. 1a

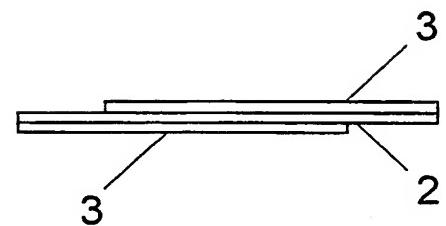


Fig. 1b

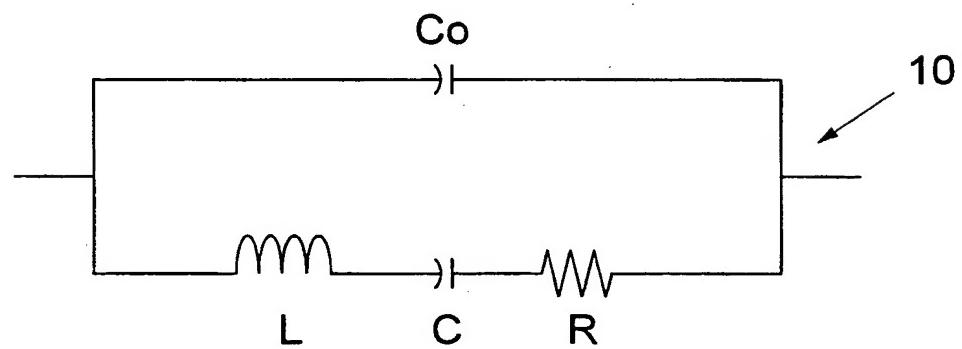


Fig. 2

SUBSTITUTE SHEET (RULE 26)

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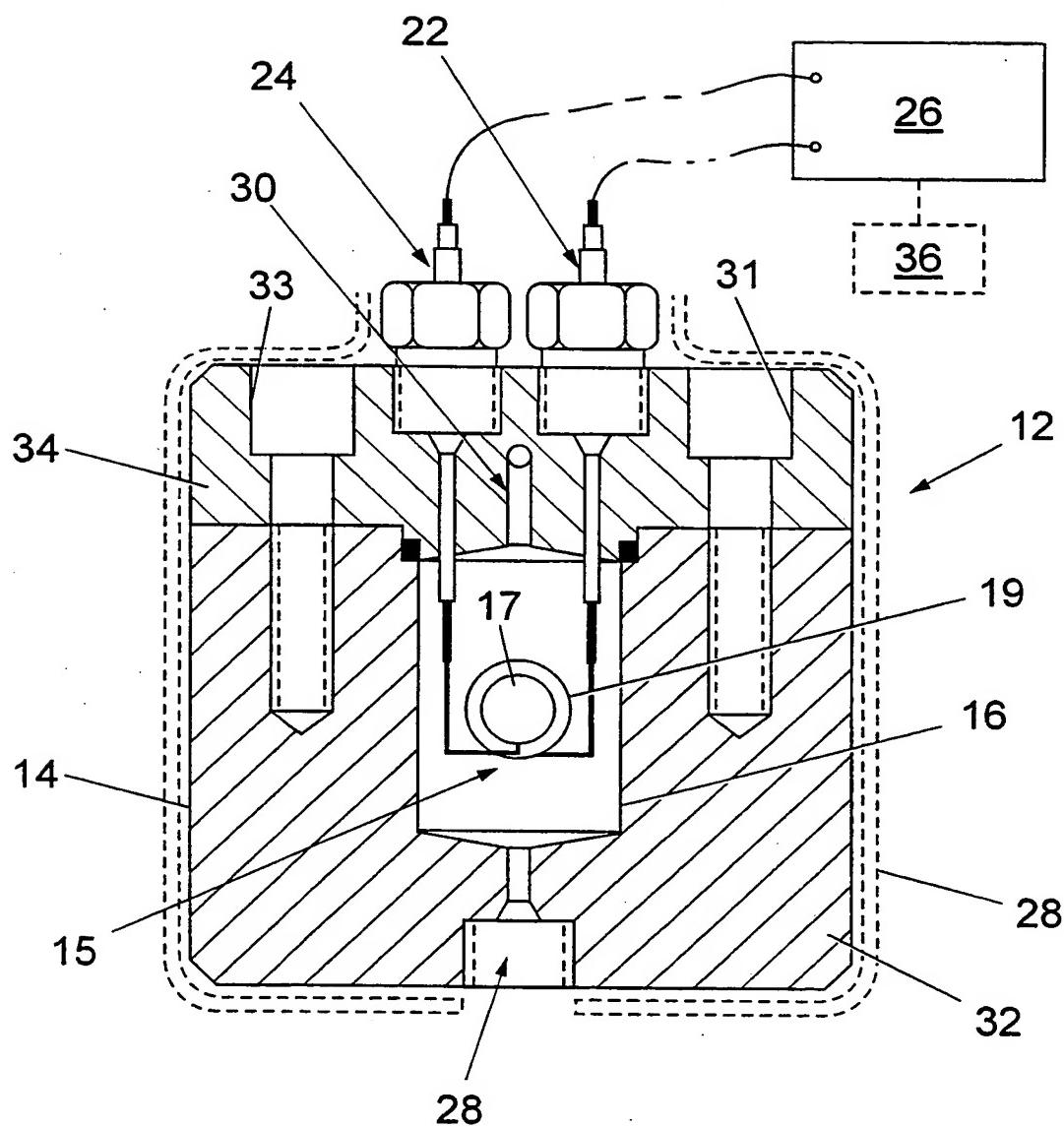


Fig. 3

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3 / 3

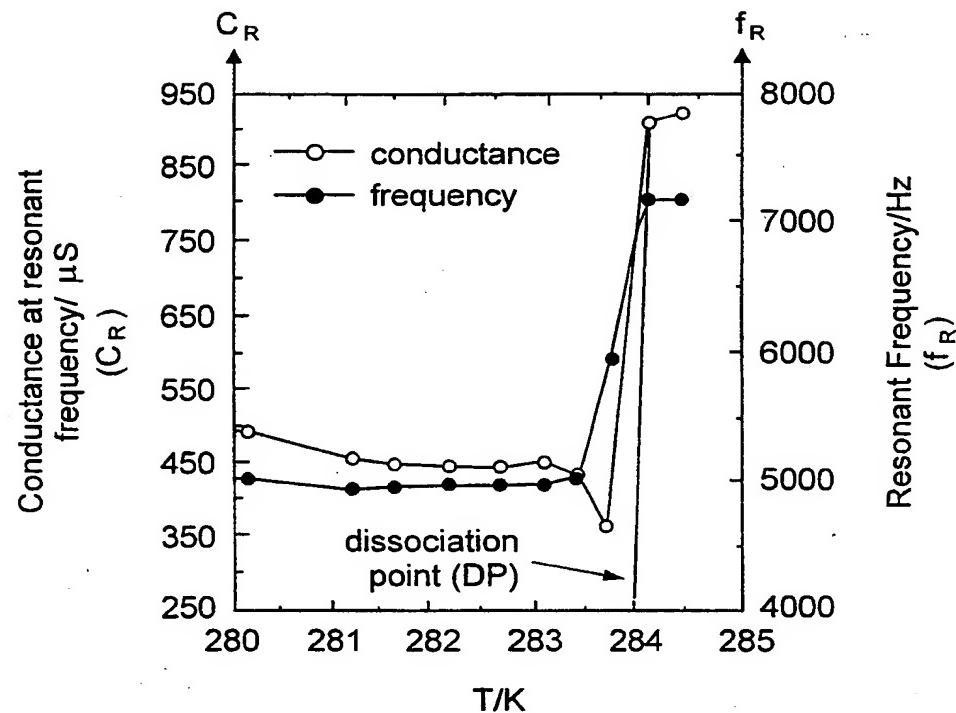


Fig. 4

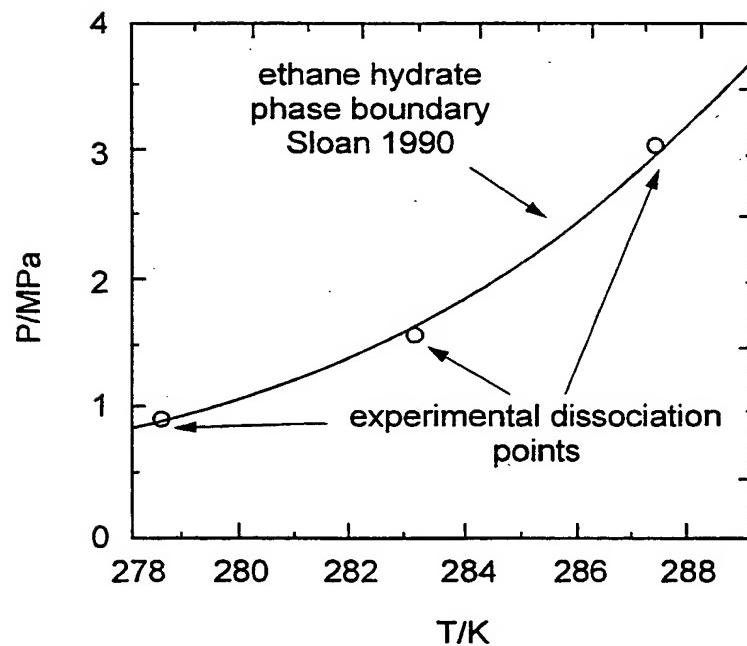


Fig. 5

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 98/01005

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 187 980 A (BLAIR DIANNA S ET AL) 23 February 1993 see abstract ---	1,26
Y	G. D. HOLDER: "hydrate dissociation pressures of (methane + ethane + water) existence of a locus of minimum pressures" J. CHEM. THERMODYNAMICS, vol. 12, no. 7, 1980, LONDON, GB, pages 1093-1104, XP002071472 see page 1095, paragraph 3 - page 1097, paragraph 2; figure 1 ---	1,26



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

Date of mailing of the international search report

14 July 1998

14/08/1998

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/01005

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	A. DANESH: "hydrate equilibrium data of methyl cyclopentane with methane or nitrogen" TRANS. ICHEM.E, vol. 72, no. a, 1994, pages 197-200, XP002071473 see page 197, right-hand column, last paragraph - page 199, left-hand column, paragraph 2; figures 1-3 ---	1
A	US 5 151 110 A (BRINKER CHARLES J ET AL) 29 September 1992 see abstract; figure 1A ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 173 (P-469), 18 June 1986 & JP 61 023955 A (MITSUBISHI DENKI KK), 1 February 1986, see abstract ---	1
A	ALFONSO L ET AL: "A QUARTZ CRYSTAL MICROBALANCE TO DETERMINE ENTHALPIES OF SUBLIMATION AT INTERMEDIATE TEMPERATURES BY THE KNUDSEN EFFUSION METHOD" MEASUREMENT SCIENCE AND TECHNOLOGY, vol. 5, no. 1, 1 January 1994, pages 51-54, XP000425430 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/GB 98/01005

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5187980	A 23-02-1993	NONE		
US 5151110	A 29-09-1992	US 5589396 A US 5224972 A		31-12-1996 06-07-1993